

D E C L A R A T I O N

In the matter of U.S. Patent
Appln. Ser. No. 09/374,344
in the name of TOTO LTD.

I, KONNO Akio, of Kyowa Patent and Law Office, 2-3,
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that I am thoroughly conversant with both the Japanese
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I further declare that all statements made herein of
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SPECIFICATION

1. TITLE OF THE INVENTION

[Title of the Invention]

Antifogging transparent member

[Claims]

1. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.
2. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function thereon.
3. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.
4. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon, via a layer which prevents diffusion of alkali-modified ingredient in the substrate.

5. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents diffusion of alkali-modified ingredient in a glass substrate.

6. The antifogging transparent material in either of claim 4 and claim 5, wherein the layer which prevents diffusion of alkali-modified ingredient is made of a metal having an electron capturing effect.

7. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon, via a resin binder layer.

[Detail description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an antifogging transparent member suitable for glass plates of automobiles, trains, airplanes, and the like, mirrors of bathrooms and lavatories, optical equipments, windowpanes of buildings, cathode ray tubes, and the like.

[0002]

[Description of Prior Art]

Glass in as-manufactured state shows good hydrophilicity giving a contact angle with water ranging

from 5 to 20 degrees. If the surface of a substrate is hydrophilic, the surface is sufficiently wetted with water, and no water droplet appears on the surface, which should prevents fogging.

In actual, however, polar ingredients such as lower carboxylic acid gradually adsorb onto the surface with time, and the surface is finally hydrophobicized ("Glass Surface Design", Kindai Henshusha, 1983), so the surface likely induces droplets when it contacts with water, and fogging appears.

[0003]

[Problems to be Solved by the Invention]

When glass plates of automobiles, trains, airplanes, and the like are fogged, safety driving in rain is threatened.

If the mirrors in bathrooms, lavatories, and the like are not fogged, face washing is conveniently done. If the cathode ray tubes of TVs, personal computers, and the like are not fogged, our living style becomes more comfortable such that we can take a bath while watching TV.

In this respect, an object of the present invention is to provide a transparent member that does not induce fogging for a long period.

[0004]

[Means to Solve the Problems]

For solving the above-described problems, the present invention provides an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.

In addition, the present invention provides an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.

Furthermore, the present invention provides an antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function.

[0005]

According to a favorable mode of the present invention, an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function or a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents diffusion of alkali-modified ingredient in the substrate.

According to a favorable mode of the present invention, the layer which prevents diffusion of alkali-modified ingredient is made of a metal having an electron capturing effect.

[0006]

According to a favorable mode of the present invention, an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function

thereon, via a resin binder layer.

[0007]

[Constituent of the Present Invention]

With the configuration of a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function, or a surface layer made of a resin made of photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function, or a surface layer made of a hydrophilicized inorganic material and a hydrophilic material having photocatalytic function thereon, antifogging performance sustains for a long period based on the mechanism described below.

[0008]

Owing to the substrate surface made of a hydrophilic material, the surface is uniformly wetted with water, and no water droplet appears. As a result, no local difference in refractive index occurs over the whole surface area, thus eliminating the appearance of fogging.

In addition, owing to the existence of a material having photocatalytic function on the surface of the substrate, polar ingredients in pollutants as absorbable materials, if existed, are decomposed by the photocatalyst, so the hydrophobicization is effectively prevented, which allows to sustain antifogging performance for long time.

[0009]

It is preferable to fix a layer made of hydrophilic material having photocatalytic functions or a layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents

diffusion of alkali-modified ingredient in the substrate. The reason of preference is that, for example, when the substrate is glass, the alkali-modified ingredient in the glass substrate is prevented from diffusion during firing step to cover the active centers of the material having photocatalytic function.

[0010]

By forming the layer that prevents diffusion of alkali-modified ingredient using a metal having an electron capturing effect, the photocatalytic function is improved as well as the improvement of prevention of diffusion of alkali-modified ingredient. Thus the surface hydrophobicization is further effectively prevented.

[0011]

By forming a layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function onto the surface of a transparent substrate via a resin binder layer, the material having photocatalytic function is further concentrated near to the uppermost layer, thus further effectively preventing the surface from hydrophobicization. In addition, adhesive strength between the substrate and the layer made of a resin made of a hydrophilicized photo-resistant ingredient and a hydrophilic material having photocatalytic function is increased owing to the presence of the resin binder layer.

[0012]

[Embodiments]

Embodiments of the present invention are described below referring to the drawings.

Fig. 1 shows a practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.

Fig. 2 shows other practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.

Fig. 3 shows a further practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function thereon.

Fig. 4 shows still other practical mode of the present invention, illustrating a structure of a transparent substrate, and a hydrophilic material having photocatalytic function thereon via a layer which prevents diffusion of alkali-modified ingredient within the substrate.

Fig. 5 shows still further practical mode of the present invention, illustrating a structure of a transparent substrate, and a layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function via a layer which prevents diffusion of alkali-modified ingredient within the substrate.

Fig. 6 shows yet other practical mode of the present invention, illustrating a structure of a transparent substrate, and a layer made of a resin made of a photo-resistant ingredient, which resin surface is hydrophilicized, and a hydrophilic material having

photocatalytic function thereon via a resin binder layer.

[0013]

The hydrophilic material is a material that shows hydrophilicity to a degree of difficult for contaminants to attach thereto, and that has a contact angle of less than 30 degrees with water. Concrete description of the hydrophilic material is given below.

Fig. 7 shows the relation between the contact angle with water and the likeliness of contamination determined on various kinds of resins.

The contact angle with water was determined by the method described below. A specimen was dipped into an artificial bath water (a warm water prepared by mixing human filth, lard, and soap) for three hours, as illustrated in Fig. 8, and relative gloss at near the water surface level before and after the dipping. The relative gloss was taken as an index of likeliness of contamination. The relative gloss is defined as the gloss after the dipping based on the gloss before dipping, or 1.

As seen in Fig. 7, the relative gloss became to minimum at around 70 degrees of contact angle with water, and contamination likely occurred. With the decrease in the contact angle with water, the relative gloss was improved more than the case of increasing the relative gloss. And the relative gloss reached a plateau in a domain below 30 degrees. Accordingly, the hydrophilicity becomes a degree to difficult to be contaminated if only the contact angle with water is less than 30 degrees.

[0014]

Examples of the transparent substrate are glass,

translucent alumina, and translucent plastics.

[0015]

Applicable hydrophilic inorganic material is basically an inorganic oxide, which includes a crystalline material such as partially stabilized zirconia, titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, di-bismuth trioxide, and tin oxide; and glass material such as glaze and silicone. Inorganic non-oxide is also applicable if only it shows hydrophilicity, for example, silicon nitride and silazane. When, however, in the example of Fig. 1, an inorganic oxide or an inorganic non-oxide, having a property of absorbing ultraviolet light, it is preferable to add a metal having an electron capturing effect to support the material having photocatalytic function. One or more of these inorganic hydrophilic materials may be used at a time.

[0016]

The material having photocatalytic function is a material which emits electrons and forms positive holes under irradiation of light having a specific wave length or less, thus being able to generate active oxygen. Examples of that type of material showing hydrophilicity are titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, di-bismuth trioxide, and tin oxide. One or more of these materials having photocatalytic function may be used at a time.

[0017]

The material having photocatalytic function is preferably containing a metal having an electron capturing effect. The metal having an electron capturing effect is a

metal such as Pt, Pd, Au, Ag, Cu, Ni, Co, Fe, Co, and Zn, which has a small ionization tendency and which is likely reduced by itself. One or more of these metals may be used at a time. Presence of a metal having an electron capturing effect induces an effect to suppress the degradation of photocatalytic function, which degradation occurs when alkali metal or alkali earth metal ions exist.

[0018]

The resin made of a photo-resistant ingredient is a resin having favorable photo-resistance. Examples of that type of resin are silicone resin, siloxane, resin, polysilazane resin, and fluororesin.

[0019]

The layer preventing diffusion of alkali-modified ingredient in the glass substrate is a layer which prevents the diffusion of alkali-modified ingredient in the glass substrate to the uppermost layer to contact with a material having photocatalytic function thus to degrade the photocatalytic function.

The alkali-modified ingredient is an alkali metal or an alkali earth metal such as sodium, potassium, calcium, and magnesium.

The material of the layer preventing diffusion of alkali-modified ingredient in the glass substrate is basically arbitrary material if only the material has the above-described function. Examples of that type of material are alumina, silica, calcium fluoride, cerium oxide, lanthanum oxide, zirconium oxide, yttrium oxide, zinc sulfate, tantalum oxide, silicon oxide, tin oxide, germanium, tellurium, lanthanum fluoride, platinum, gold,

silver, copper, zinc, iron, nickel, cobalt, and palladium.
[0020]

When platinum, gold, silver, copper, zinc, iron, nickel, cobalt, or palladium is used in the layer preventing the diffusion of alkali-modified ingredient in the glass substrate, the photocatalytic function is enhanced because these elements have an electron capturing effect. Accordingly, the addition of these elements is preferable because the surface hydrophobicization is further effectively prevented.

When, in the case that the glass substrate is made of a low melting point material such as soda glass, a layer made of high purity silica is used in the layer which prevents the diffusion of alkali-modified ingredient in the glass substrate, the sinking of a material having photocatalytic function into the substrate during the firing stage is reduced, thus making the material having photocatalytic function concentrate to the uppermost surface to improve the photocatalytic function. The use of high purity silica layer is preferable because the surface hydrophobicization is further effectively prevented.

[0021]

The resin binder layer shown in Fig. 6 may be the same kind of resin with that of the surface made of a photo-resistant ingredient, and may not be necessarily the same kind therewith. Therefore, more inexpensive resin may be used for molding. As for the resin binder, both of an inorganic binder such as silicone and an organic binder such as thermosetting resin, photo-setting resin, and thermoplastic resin are applicable.

[0022]

The following is an outline of a method for manufacturing an anti-contaminant member shown in Figs. 1 through 6.

First, the description is given to the case of Fig. 1, wherein the transparent substrate is quartz glass, the resin made of a photo-resistant ingredient having a hydrophilicized surface is a siloxane resin derivative to which the surface hydrophilicization is conducted by the method described later, the hydrophilic material having photocatalytic function is anatase titanium oxide, and the anatase titanium oxide contains copper as a material having an electron capturing effect.

In that case, the manufacturing method of the member basically comprises the steps of: preparing a mixed liquid of anatase titanium oxide sol and a solution containing copper ion; preparing an applying liquid by adding siloxane resin, a diluent, and a curing agent to the mixed liquid; applying the applying liquid onto a quartz glass; firing the quartz glass to obtain an intermediate member; irradiating light containing ultraviolet light to the intermediate member to decompose or oxidize a portion made of alkyl and the like in the siloxane resin layer formed on and exposed to the surface, thus hydrophilicizing the surface of the intermediate member.

[0023]

It is preferable that anatase titanium oxide sol is fully dispersed in the suspension. To do this, the dispersion is done in acidic or alkaline state because the anatase titanium oxide has an isoelectric point at pH 6.5.

Surface active agent or dispersant (deflocculating agent) may be added to improve the dispersability. Generally, water, ethanol, and propanol are often used as the solvent to disperse the anatase titanium oxide sol.

[0024]

The solution containing copper ion is preferably a solution of soluble copper compound such as cupric acetate and cupric sulfate. For the case of metal having an electron capturing effect, other than copper, soluble solution of silver nitrate, silver sulfate, silver lactate, and silver acetate are preferable because of simplicity of mixture treatment. As for the solvent used in a solution containing copper ion, it is preferable to use the same kind of material with anatase titanium oxide sol suspension water, though ethanol, and propanol are applicable.

[0025]

In the step for mixing anatase titanium oxide sol suspension with a solution containing copper ion, pH of the solution containing copper ion is preferably adjusted to almost the same with pH of the anatase titanium oxide sol suspension. The reason is that the change in pH of the anatase titanium oxide sol suspension is smaller, thus the pH of the solution containing copper ion does not significantly degrade the dispersability of the anatase titanium oxide sol in the suspension.

[0026]

After mixing the anatase titanium oxide sol suspension with the solution containing copper ion, a light containing ultraviolet light may be irradiated thereto. Irradiation of light containing ultraviolet light makes copper ion

photoreduce to fix onto the anatase titanium oxide particles, so the photocatalytic function is improved.

The light containing ultraviolet light is a light having sufficient energy for reducing metal ion such as copper ion which has an electron capturing effect.

[0027]

It is preferable to prepare the applying liquid by adding siloxane resin, diluent, and curing agent in this sequent order because of giving least possibility of coagulation.

[0028]

The method for applying the liquid onto the surface of quartz glass is basically arbitrary one. An applicable method for applying the liquid includes spray coating method, roll coating method, and dip coating method.

[0029]

The step for heat treatment in that case may be conducted at a low temperature below 100°C for a long period, or may be conducted at 100°C or above and below the heat resistant temperature of the photo-resistant ingredient (Si-O bond section in siloxane resin, for example) in the resin and below the heat resistant temperature of the substrate (quartz glass) for a short period. Generally, particles made of a material having photocatalytic function have heavier specific gravity than a resin containing photo-resistant ingredient, it is preferable to conduct heat treatment at 100°C or above and below the heat resistant temperature of the photo-resistant ingredient (Si-O bond section in siloxane resin, for example) in the resin and below the heat resistant temperature of the substrate

(quartz glass) because the particles made of a material having photocatalytic function concentrate to the upper layer section made of a material having photocatalytic function, and because the time for hydrophilicization step is shortened by irradiating light containing ultraviolet light onto the surface of the intermediate member, thus oxidizing or decomposing the section structured by alkyl and the like in the siloxane resin layer which is formed on and exposed to the surface.

[0030]

The step for decomposition or oxidization of R section comprising alkyl and the like in siloxane resin formed to expose on the surface of intermediate member presumably proceeds following the reaction shown below under irradiation of light containing ultraviolet light.

[0031]

[Formula 1]

[0032]

The light containing ultraviolet light means a light which has sufficient energy for actuating electrons from valence electron band to conduction band in a material having photocatalytic function. For the case of anatase titanium oxide, light containing a light of less than 400 nm of wavelength is irradiated.

[0033]

Referring to Fig. 2, an illustration is given in the case that the transparent substrate is quartz glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, basically the steps include application

of precursor of anatase titanium oxide such as titanium alkoxide onto quartz glass, followed by firing thus applied glass.

[0034]

The precursor of anatase titanium oxide means a material which changes into anatase titanium oxide after fired. Examples of the precursor of anatase titanium oxide are organic titanate such as titanium alkoxide and inorganic titanate such as titanium sulfate. Use of that type of precursor of anatase titanium oxide is preferable because it is applied uniformly onto substrate.

[0035]

The following description on the step to apply a precursor of anatase titanium oxide onto a quartz glass uses titanium tetraethoxide ($(C_2H_5O)_4Ti$), which is a kind of titanium alkoxide, as the precursor of anatase titanium oxide.

[0036]

First, a coating solution is prepared by adding a diluent and hydrochloric acid to titanium tetraethoxide.

A preferable diluent is alcohol such as ethanol and propanol owing to the easiness of handling. Water should be minimized as far as possible. Existence of plenty of water explosively accelerates the hydrolysis of metallic alkoxide, which causes crack generation.

Addition of hydrochloric acid is given to prevent crack generation in succeeding steps of drying and heat treatment.

[0037]

Next, a coating solution is applied onto the substrate. Flow coating method is simple and preferable for applying

metallic alkoxide. Flow coating is preferably conducted in dry air. The dry air does not mean the one free of water but means less water content than ordinary atmospheric air. If the coating is done in ordinary atmospheric air, hydrolysis is excessively accelerated by the moisture in air so that the control of film thickness becomes difficult. For the case of titanium tetraethoxide, preferable coating weight per single cycle of application is 100 μ g or less of titanium oxide per cm^2 from the point of prevention of crack generation.

[0038]

A titanium oxide film is formed after drying the applied substrate in dry air for 1 to 10 min. The principle of obtaining titanium oxide in the above-described steps is the following. First, titanium tetraethoxide as the starting material is hydrolyzed by water in dry air during the flow coating to yield a hydroxide of titanium. Then, dehydration condensation occurs during the drying step to yield amorphous titanium oxide on the substrate. The titanium oxide particles generated have individual particle size of several nanometers and are high purity. Consequently, thus obtained titanium oxide is sintered at a lower temperature than titanium oxide prepared by other methods.

[0039]

When the applied product obtained from the above-described procedure is fired at 400°C or above, the amorphous titanium oxide crystallizes to yield an antifogging transparent member having anatase titanium oxide film which is dense and hydrophilic structure.

[0040]

Next description is in the case that, in Fig. 3, the transparent substrate is quartz glass, the hydrophilic inorganic material is a low melting point glass ingredient, the hydrophilic material having photocatalytic function is anatase titanium oxide, and the anatase titanium oxide contains copper as a material having an electron capturing effect.

In that case, the basic preparation steps are a sequent order of: a step for preparing a mixed liquid by mixing anatase titanium oxide sol with a solution containing copper ion; a step for preparing an applying liquid by mixing a low melting point glass ingredient to thus prepared mixed solution; a step for applying thus prepared applying liquid onto a quartz glass; and a step for firing the glass.

[0041]

The low melting point glass means a glass composition having lower melting point than the substrate. In this case, the glass composition has lower melting point than that of quartz glass.

[0042]

The following description is for Fig. 4 wherein the transparent substrate is soda glass, the layer to prevent diffusion of alkali-modified ingredient in the substrate is silica glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, the basic steps includes: a step for applying a precursor of silica glass such as silicon alkoxide onto a soda glass; a step for applying a alkoxide onto a quartz glass; and a step for firing the glass.

[0043]

The step for applying the precursor of silica glass such as alkoxide onto the soda glass is performed by the following procedure.

First, the coating solution is prepared by adding a diluent, water, and hydrochloric acid to tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$).

The reason of addition of water is that alkoxysilane is stable compared with alkoxide of transient metal such as titanium so that it is hard to induce hydrolysis, thus enhancement of hydrolysis is needed.

Since the prepared coating solution generates heat under water addition, the flow coating onto the substrate is recommended to begin after allowed the coating solution to stand for about 1 hour.

[0044]

The following description is for Fig. 5 wherein the transparent substrate is soda containing translucent alumina, the layer to prevent diffusion of alkali-modified ingredient in the substrate is silica glass, the hydrophilic inorganic material is silica glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, the basic steps include: a step for applying silica component such as silicon alkoxide onto the soda-containing translucent alumina; a step for applying a mixture of massive silica such as frit and anatase titanium oxide sol onto the applied silica component; and a step for firing them.

[0045]

The following description is for Fig. 6 wherein the transparent substrate is soda glass, the resin binder layer is siloxane resin, the resin made of a photo-resistant ingredient which surface is hydrophilicized is a siloxane resin derivative which is hydrophilicized on the surface thereof by a method described later, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In that case, basic procedure for preparation comprises: a step for applying a mixed liquid of siloxane resin and a curing agent onto the soda glass; a step for mixing anatase titanium oxide sol with a solution containing copper ion; a step for adding siloxane resin, a diluent, and a curing agent to the mixed solution to prepare an applying liquid; a step for applying thus prepared applying liquid onto the soda glass; a step for firing the soda glass to obtain an intermediate member; a step for irradiating light containing ultraviolet light to the intermediate member thus inducing decomposition or oxidization of a portion made of alkyl and the like in the siloxane resin layer formed on and exposed to the surface to make the member hydrophilic.

[0046]

The following is effects of the above-described embodiments on the basis of concrete evaluation experiments.

(Evaluation experiment 1)

Tetraethoxysilane, 36% hydrochloric acid, pure water, and ethanol were mixed together at respective weight ratio of 6 : 2 : 6 : 86. The mixture was allowed to stand for 1

hr, then the mixture was applied onto the surface of soda glass by the flow coating method to obtain an intermediate member P.

Titanium tetraethoxide and ethanol were mixed at respective weight ratio of 1 : 9, to which 36% hydrochloric acid was further added at 10 wt.% to the titanium tetraethoxide to obtain a coating liquid. The coating liquid was applied onto the surface of the intermediate member P in dry air by the flow coating method. The coating weight per application was adjusted to 45 ug-titanium oxide per square centimeter.

After then, the applied intermediate member P was dried in dry air for a period of from 1 to 10 min, followed by firing at 500°C to obtain a specimen Q.

The surface of the specimen Q was applied by 1 wt.% copper acetate aqueous solution using the spray coating method. The light of 20W BLB fluorescent lamp was irradiated onto the surface of Q from a distance of 20 cm to obtain a specimen A. Observation of the specimen A proved to have a sufficient translucent property.

The characteristics of antifogging performance, contact angle with water, anti-bacterial performance, anti-odor property, and anti-abrasion property were evaluated for the specimen A, and also for a soda glass and the intermediate member P for comparison.

[0047]

As for the antifogging property, an as-prepared specimen and a specimen after irradiated by BLB fluorescent lamp for 1 month were treated by breathing method to provide fog on the surface thereof, then the presence/absence of

water droplet on the surface was checked under a microscope.

For the contact angle with water, an as-prepared specimen and a specimen after irradiated by BLB fluorescent lamp for 1 month were determined for the angle of contact using a contact angle meter.

The result is shown in Table 1.

[0048]

[Table 1]

[0049]

Since the soda glass substrate has a significantly hydrophobic property giving 50 degrees of contact angle with water, the soda glass after prepared the specimen showed the generation of water droplets. To the contrary, the specimen A and the intermediate member P did not show water droplet on the surface because they have a small contact angle with water, less than about 1 degree, and they are sufficiently hydrophilicized.

After irradiating BLB fluorescent lamp for 1 month, the soda glass substrate and the intermediate member P were hydrophobicized to a significant degree, giving 53 degrees and 49 degrees of contact angle with water, respectively, and generated water droplets. On the specimen A, however, the contact angle with water was 3 degree, which indicated a progress of hydrophilicization, and no water droplet was observed.

[0050]

As for the anti-bacterial property, the evaluation was given using W3110 strain of *Escherichia coli*.

A glass plate (100 x 100) on which 0.15 ml of bacterial

liquid (10000 - 50000 CFU) was dropwise added was attached to the uppermost surface of each of the above-described specimens which were preliminarily sterilized by 70% ethanol. White light (3500 lux) was irradiated to each of the specimens for 30 min. The bacteria liquid was wiped off using a sterilized gauze, which was then recovered into 10 ml of physiological salt solution. Thus the survival rate was determined to use as the index of evaluation. The criteria of index are listed below.

+++ : Less than 10% of survival rate of *Escherichia coli*.

++ : Ten percent or more and less than 30% of survival rate of *Escherichia coli*.

+ : Thirty percent or more and less than 70% of survival rate of *Escherichia coli*.

- : Seventy percent or more of survival rate of *Escherichia coli*.

The evaluation of soda glass substrate and of intermediate member P was (-), and the specimen A showed (+++) of good evaluation.

[0051]

The evaluation of odor prevention was determined by measuring R30(L) value. The term R30(L) means the rejection rate of odor ingredient after the irradiation of light. In concrete terms, the steps for determining R30(L) are: placing a specimen in an 11 liter glass container facing the surface covered with antifogging film to the light source (4 w BLB lamp) at a distance of 8 cm; injecting methylmercaptan gas into the container to create 3 ppm of initial concentration; irradiating light against the specimen surface for 30 min; then determining the change in

concentration of the gas.

The value of R30(L) was less than 10% for the soda glass and the intermediate member P, and was 90% or more for the specimen A.

Regarding the anti-abrasion characteristic, a rubbing abrasion was given to the surface of each specimen using a plastics eraser, then the change of appearance was observed. The criterion of the evaluation on the anti-abrasion characteristic is given below.

- ◎: No change occurred after 40 cycles of traverse.
- : Flaw appeared and the surface layer was separated after traversing cycles of 10 or more and less than 40.
- △: Flaw appeared and the surface layer was separated after traversing cycles of 5 or more and less than 10.
- ×: Flaw appeared and the surface layer was separated after less than 5 cycles of traverse.

Favorable results (◎) were obtained for all of the soda glass substrate, the intermediate member P, and the specimen A.

[0053]

(Evaluation experiment 2)

A solution of siloxane resin containing a curing agent was applied onto a transparent acrylic plastics substrate (10 cm square). The substrate was treated by heat at 140C to prepare an intermediate member S. A liquid was prepared by: mixing a nitric acid suspension of titanium oxide sol having 0.01 μ m of average suspended particle size, 3 wt.% of aqueous solution of copper acetate, and siloxane resin at a weight part equal to that of solid titanium oxide; diluting the mixture with propanol; further adding a curing agent

to the mixture; applying thus prepared mixture onto the surface of the intermediate member S; then heat-treating the intermediate member S at 140°C to obtain an intermediate member T. A ELB lamp light was irradiated against the intermediate member T for 5 days to obtain a specimen B. For the specimen B and an acrylic plate as a reference material.

For each of the specimen and the intermediate member, evaluation was given on the antifogging property, the contact angle with water, the anti-bacterial property, the odor preventive performance, and the anti-abrasion property. The method of evaluation was the same with that used in Evaluation experiment 1.

[0054]

For the acrylic plate, the contact angle with water showed 70 degrees for both before and after 1 month of BLB fluorescent lamp light irradiation, which suggested that the plate was hydrophobicized to significant degree. In fact, the acrylic plate showed generation of water droplets. To the contrary, the specimen B showed a small contact angle with water, or 3 to 9 degrees. The specimen was sufficiently hydrophilicized on its surface, and no water droplet was observed on the surface.

For the anti-bacterial property, the acrylic plate gave the result of (-), and the specimen B provided a good result of (+++).

As for the anti-odor property, the acrylic plate gave the value of less than 10%, and the specimen B provided a good result giving more than 90%.

Regarding the anti-abrasion property, both the acrylic

plate and the specimen B showed favorable result of oo mark.

[0055]

[Effect of the Invention]

Favorable anti-fogging performance is sustained for a long period by covering the transparent substrate with: a layer made of a hydrophilic material having photocatalytic function thereon; or a layer made of a resin made of a photo-resistant ingredient hydrophilicized at the surface thereof and a hydrophilic material having photocatalytic function; or a layer made of an inorganic material having hydrophilic material and a hydrophilic material having photocatalytic function.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 shows an example of the present invention.

[Fig. 2]

Fig. 2 shows other example of the present invention.

[Fig. 3]

Fig. 3 shows further example of the present invention.

[Fig. 4]

Fig. 4 shows still other example of the present invention.

[Fig. 5]

Fig. 5 shows still further example of the present invention.

[Fig. 6]

Fig. 6 shows yet other example of the present invention.

[Fig. 7]

Fig. 7 shows the relation between the contact angle with water and the likeliness of contaminant adhesion.

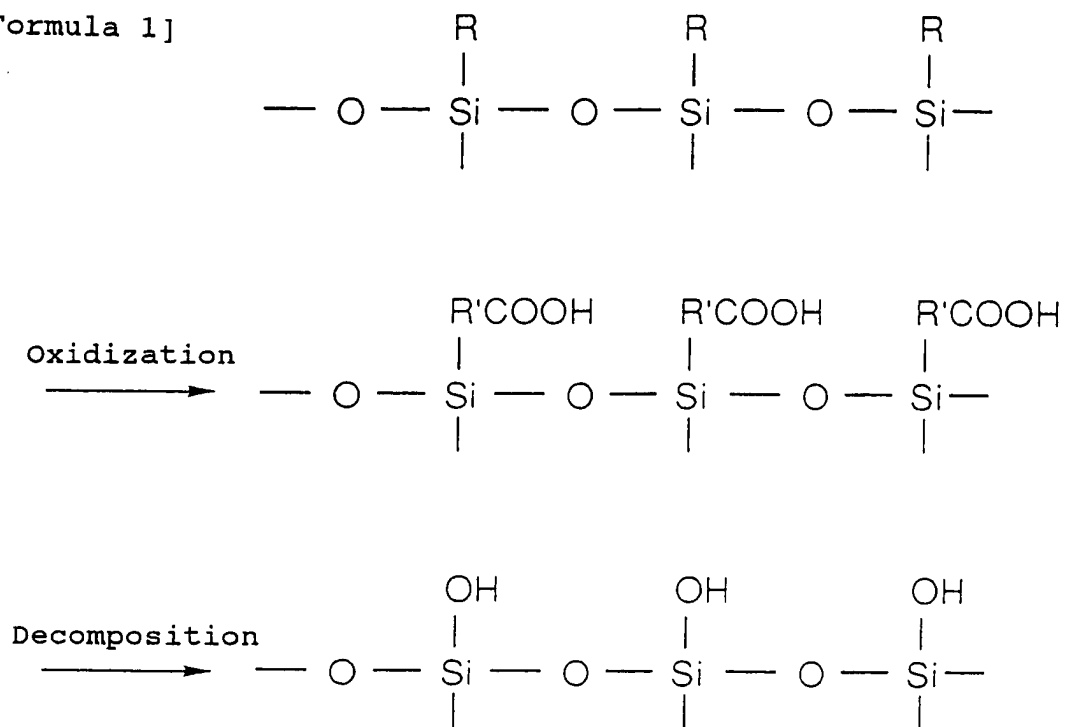
[Fig. 8]

Fig. 8 illustrates an evaluation device for anti-contamination property.

[Description of the Reference Symbols]

- 1: transparent substrate
- 2: resin made of a photo-resistant ingredient, which surface is hydrophilicized
- 3: hydrophilic material having photocatalytic function
- 4: inorganic material having hydrophilic property
- 5: layer to prevent diffusion of alkali modified ingredient in substrate
- 6: resin binder layer
- 7: filth
- 8: artificial bath water
- 9: specimen

[Formula 1]



[Table 1]

	After preparing specien		After 1 month has passed	
	Contact angle to water (°)	Antifogging property	Contact angle to water (°)	Antifogging property
Specimen A	10	Absence of water droplet	3	Absence of water droplet
Soda glass	50	Absence of water droplet	53	Absence of water droplet
Intermediate member P	9	Absence of water droplet	49	Absence of water droplet

Fig. 1

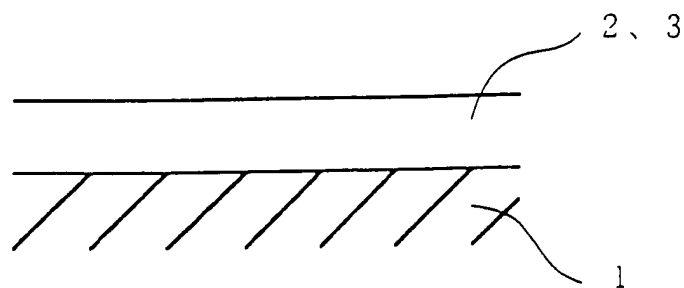


Fig. 2

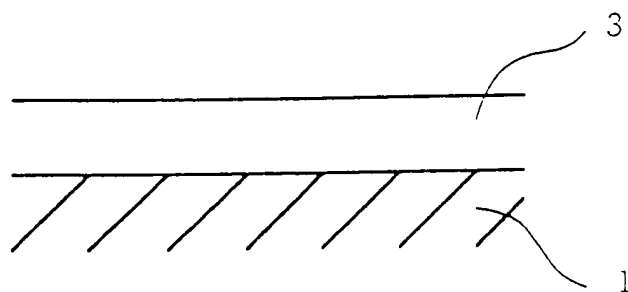


Fig. 3

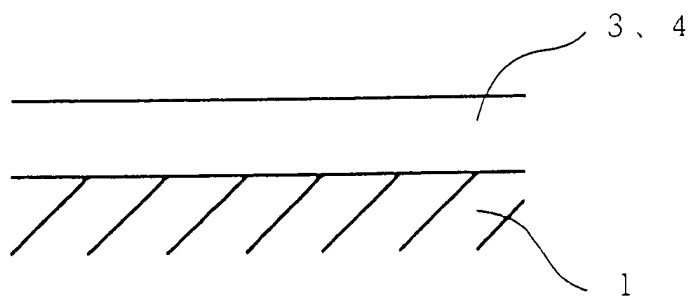


Fig. 4

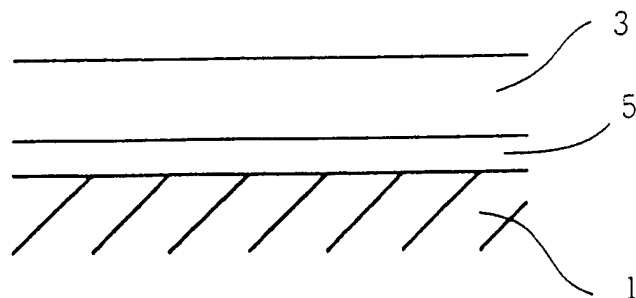


Fig. 5

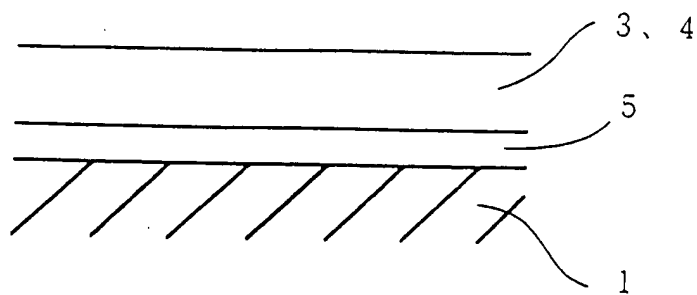


Fig. 6

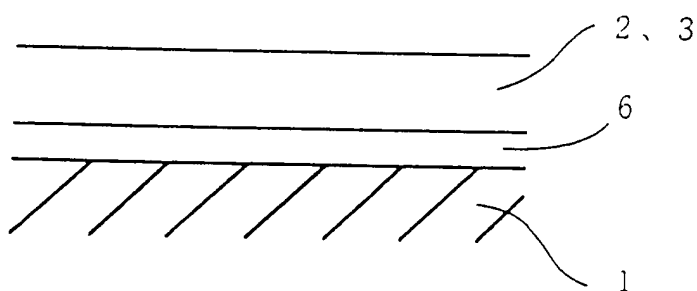


Fig. 7

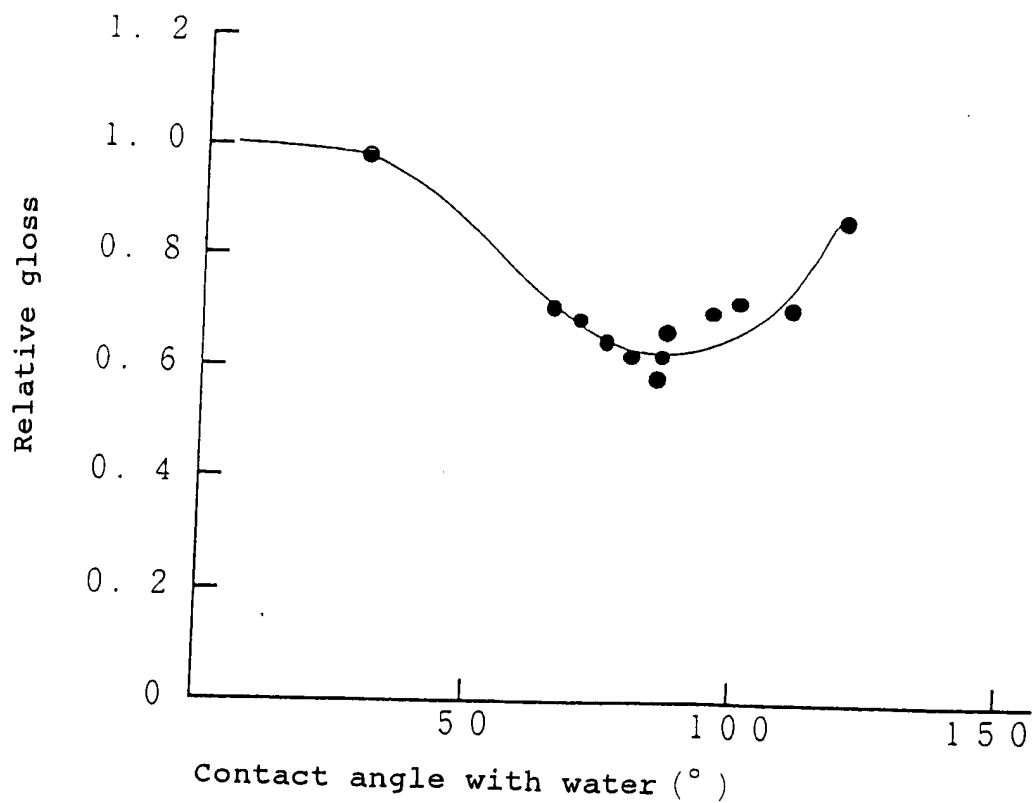
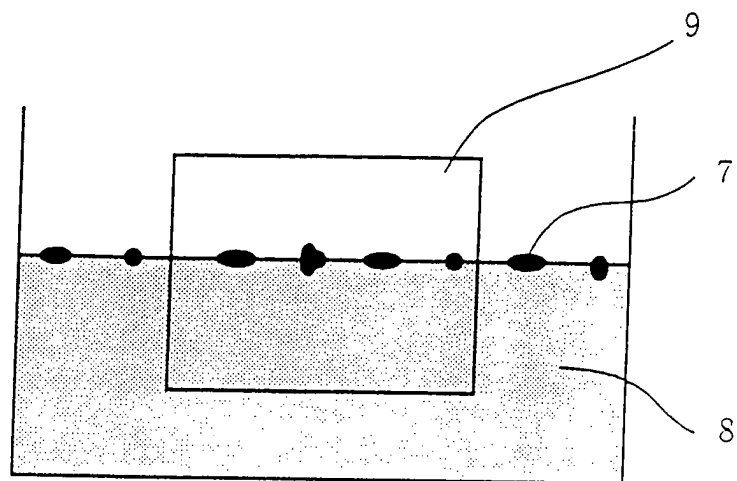


Fig. 8



ABSTRACT

[Object]

To provide an antifogging transparent member sustaining favorable antifogging property for a long period.

[Constituent]

An antifogging member comprises a transparent substrate (1), and a surface layer made of a hydrophilic material (3) having photocatalytic function thereon; or comprises a transparent substrate, and a surface layer made of a resin (2) made of a photo-resistant ingredient hydrophilicized at the surface thereof and a hydrophilic material having photocatalytic function; or comprises a transparent substrate, and a surface layer made of an inorganic material having hydrophilic material and a hydrophilic material having photocatalytic function.

[Selected Drawing]

Fig. 1

photocatalyst.

[0011]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic catalyst is formed on the substrate.

[0012]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material is formed on the substrate.

[0013]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material is formed on the substrate, while an exposed surface is made of a non-photocatalytic hydrophilic material.

[0014]

According to a preferred mode of the present invention, an intermediate layer is sandwiched between the substrate and the surface layer.

[0015]

According to a preferred mode of the present invention, the non-photocatalytic hydrophilic material is a hydrophilicized photo-resistant resin.

[0016]

According to a preferred mode of the present invention, the non-photocatalytic hydrophilic material is an inorganic amorphous material.

[0017]

According to a preferred mode of the present invention,